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A study of Kentucky fluorite

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A STUDY OF KENTUCKY FLUORITE.

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The Kentucky fluor-spar district, embracing Crittenden, Livingston and Caldwell counties in western Kentucky, is the only section in America, with the exception of southern Illinois, where fluor-spar is mined, ground, and shipped in quantity. The fluor-spar is also associated with rich surprises in zinc and lead ores.

Before proceeding to a study of the district in question, it may be well to give a brief description of the mineral itself.

Fluorite or fluor-spar as it is commonly called, is composed of calcium 51.1% and fluorine 48.9%, corresponding to the chemical formula CaF_2; chlorine is sometimes present in minute quantities. It occurs in cubic crystals and in compact and granular forms; is sometimes fibrous. It ranges in color from white through yellow, light green, purple, blue, and more rarely rose red. The colors are usually bright and in massive varieties, they are frequently banded.

Fluorite usually flies to pieces violently when heated before the blowpipe, but when pulverized it can be fused, giving forth the yellowish red flame characteristic of lime. When broken into fragments and heated moderately in a closed tube, it phosphoresces, emitting in some varieties a yellowish light, in others a beautiful green glow. A hammer blow is sufficient to cause a mass of fluorite to exhibit phosphorescence for hours.

It frequently forms the gange or matrix of the metallic ores in mines, especially in lead mines in limestone, and it is found occurring in veins in the older gneissic, granitic and slaty rocks.

HISTORY OF THE DISTRICT.

The ore deposits of this district have been known to settlers since early in the last century. That it was known to the Indians, is proved by the discovery, in some pre-historic mounds of this region, of fluor-spar, shaped into ornaments. The earliest scientific mention of its occurrence is found in the first volume of the American Journal of Science (1818), which describes specimens obtained in the vicinity of Shawneetown, Illinois, by Mr. Joseph Baldwin. In the same publication, --July, 1852-- Prof. S.J.Brush visited the mines that had been opened near Rosiclare, Illinois, "An immense amount of remarkably fine quality of fluor-spar," he remarks, "could be obtained from these veins should there be a demand for it in the arts."

In the Illinois Geological Reports, 1858, are notes of Dr. Norwood upon the Rosiclare lead mines and from these it appears that galena and fluor-spar were first discovered in this region by the sinking of a well. Mining was begun then and kept up until the civil war. ~~The first~~ The first attempt to mine on the Kentucky side of the Ohio river, was made by a company headed by President Andrew Jackson. The effects of the civil war and the fall in the price of lead both exercised an unfavorable influence,,but, from what can be seen there now, it is evident that bad management and ignorance of proper methods of mining have been important factors in retarding the systematic developement of the region. Much money has been spent ill-advisedly, and resulting financial disaster has discouraged capitalists. The mines were originally worked for lead alone, the fluor-spar having little commercial value. Of late years conditions have been reversed; an increasing market for fluor-spar as a flux in smelting and for glass making has been developed; and during the past decade the mines have been worked primarily for the spar, the lead being a side product. As compared with the galena of other parts of the Mississippi Valley region, it is exceptional, however, as containing a small

but persistent amount of silver, a sample from the Belt mine near Marion, Kentucky, running as high as 7.52 ounces to the ton. But on an average the galena carries about two ounces to the ton.

PRODUCTION.

No records are obtainable for the actual production for the period before the year 1891. The production of fluor-spar from Illinois and Kentucky mines for the years 1891 to 1903.

Year.	Tons.	Value.	Per ton.
1891.	6320.	$38000.	$6.00.
1892.	9000.	54000.	6.00.
1893.	9700.	63050.	6.50.
1894.	6400.	38400.	6.00.
1895.	4000.	24000.	6.00.
1896.	6000.	48000.	8.00.
1897.	4379.	36264.	7.65.
1898.	12145.	86985.	7.16.
1899.	24030.	152655.	6.35.
1900.	19586.	113803.	5.81.
1902.	27127.	143520.	5.29.
1903.	37450.	194740.	5.20.

The Kentucky mines producing about 80% during the years 1898 to 1903.

The figures above show that the demand for fluor-spar is rapidly increasing and from recent reports more was produced during the year 1904 than ever before.

TOPOGRAPHY AND GEOLOGY.

The deposits of fluor-spar in western Kentucky are extremely interesting. These deposits occur in the low-lying country traversed by the Ohio and Cumberland rivers and their tributaries. They are associated with the St.Louis limestone of the lower carboniferous age, and belong to the same group as the Rosiclare deposits, of Hardin county, Illinois. The limestones have received local names from the places where they are best developed and exposed, hence the name of St.Louis limestone.

This region is a rolling country of low broken ridges, generally with rounded surfaces and partly covered with timber, and with an irregular drainage system. Except along the Ohio river, actual rock outcrops are not frequent. Where limestone forms the rock-surface there is often an accumulation of from twenty to forty feet of soil and red clay, resulting from the chemical solution of rocks. where sandstone forms the surface the soil accumulation is generally thin. This rock caps the higher bluffs and ridges, and also along the west side of the veins,where there is no prominent elevation. In such cases the loose surface materi--al over the rock surface will suddenly deepen from a few feet on one side to twenty or thirty feet on the other side of the lode, without show ing any discrepancy of surface. In the , "Trans. Amer. Inst. Min. Eng." 1892, "Emmons" explains this as follows:-"The vein fissures, are evidently a system of fault-planes whose down throw is on the hanging or west side, strike being made from 5° to 40° east of north. The apparent irregularity presented by the fact that the down throw side of the vein is now generally higher than the raised side," he explains it thus; "In the gereral lev--elling of the country by earlier erosion, the sandstones have been entirely removed from the raised side; in later erosion, which has been mainly a solution of the exposed limstone surfaces by atmoapheric waters, the sandstone on the downthrow sides have acted as protecting caps against erosion which has eaten away the limestones."

The ores occurring in well defined fault ~~veins~~ planes and fissures, which intricately penetrate the district, extending for many miles in length and varying in width from three feet to thirty feet.

There are at least thirty faults in the district, with maximum displacements of from 400 to 1400 feet and traceable for distances of from 2 to 20 miles or more.

As a rule the fault lines are practically straight, apparent slight deflection in the course being generally due chiefly to the dip of the fault planes, which is usually considerable, upon the line of outcrop over the undulating surface.

Many of the faults are associated or connected with a series ~~of~~ of subsidiary fractures and faults, whose displacement rarely exceeds 200 feet, they may be distinguished as main faults. Of the subsidiary fissures, there are probably hundreds, and it is said that many of them will prove more productive, for equal lengths, than the veins in the main faults.

The formation of the mica-peridotite dikes, of which seven or eight are known in Crittenden county, is believed to have taken place prior to the extensive faulting of the region. Quoting from "Contributionsto Economic Geology 1892," Government report; They were probably produced by an accumulation of matter within this portion of the crust of earth, causing its elevation and fracturing and subsequent intrusion of the igneous masses. The strain on the continuity of the strata produced by their elevation caused the relatively brittle limestone to part along certain lines and form fissures.

Most of the veins show distinct evidence of movement either in the displacement of the beds on the opposite sides of the fissure or in shearing with or without well defined slickensiding.

VEIN MINERALS.

Fluorspar is the most important vein mineral, as a rule it carries with it varying proportions of other minerals, principally galena, blende,

barite and calcite.

The occurrence of galena is most irregular. It is generally in large coarsely crystaline masses, entirely enclosed by and often intergrown with fluorspar. Sometimes copper pyrites are found in very small grains, entirely enclosed in the galena, in unimportant amount.

According to the testimony of miners, the proportion of galena increases in depth, being very sensibly greater between 100 and 200 feet than above. In one of the workings, continuous masses of galena of 100 tons weight are said to have been found.

The occurrence of zinc blende, which is found in many veins, occurs mainly as minute grains disseminated in the included fragments of limestone, frequently concentrated near the contact between the fragments and the inclosing fluorspar. The fine grained spalerite or blende is more abundant in some of the workings than the galena, and will prove of economic importance if a satisfactory method of separating it from the enclosed fluorite is found.

Surface waters have dissolved out caves along the walls of most of the veins, and these are lined with red mud or slime, resulting from the solution of the limestone. The water found in the mines, evidently comes mainly from the surface waters, being of inconsiderable amount in dry seasons and often flooding the mines in the wet ones.

Emmons on Manner of Formation of the Deposits. ----(Amer. Inst. Min. Eng. 1892.)

"A considerable proportion of the deposit, has been formed by replacement or substitution. The foetid character of some of the spar, which it undoubtedly inherits from the replaced limestone, the residual bituminous matter found in the vein material, and in one case a fossil found by Dr. Norwood, are proofs of this in addition to the already sufficient banded arrangement of the vein material and replaced portions of dragged in country rock. It seems probable that the original crevice, as formed by dynamic action, was relatively small, and was gradually enlarged by circulatory waters. Under varying conditions these waters

were probably at one time removing material and at another depositing it. The relation of the crystaline calcspar to the adjoining limestone wall shows at one time (before the access of surface waters) calcite was dissolved, and subsequently deposited in a crystalline form in the same place. The relation of the crystalline calespar to the fluorspar suggests that the latter may have been formed as a replacement of the former. The metallic minerals in the portion of the vein coming under observation are unimportant genetically. Their occurrence in the midst of a great vein of pure fluorspar does not necessarily imply that they were deposited freely in a large cavity, for galena crystals are often found isolated in a mass of unaltered limestone, which must have reached there by gradual exudation of solution through the surrounding rock-mass."

Emmons derives his fluorspar from the surrounding limestones, he also derives his lead and zinc the same way. He says that a chemical analysis of the limestone shows the presence of fluorine, and that it is well known that sea water contains small but appreciable quantities of it.

In Livingston county the ore is described by Norwood (Kentucky Geological Survey 1875) as occurring in a fissure between limestone and and sandstone walls. He says that the country was traversed by ~~post~~ great earth movements producing faults and open fissures.

Concerning the derivation of the ore, Norwood concludes that the ore was eliminated fromthe over lying and decomposing limestones and redeposited from the solutions in the fissures below. The order of deposition he states to be first galena, then fluorspar, and later calcite He is emphatic in stating that the theory of the derivation of the ore from above rather than below is necessary to satisfy all requirements.

All available evidence tends to the conclusion that vein deposits of some kind occur in all the fractures where either one or both walls are limestone, excepting where the fractures are occupied by peridotite dikes. These usually are accompanied by only a slight dis-

placement of the strata, and, with a single exception, are not associated with valuable minerals.

It is evident that the ores were deposited from aqueous solution, that the lead and zinc were originally deposited in the form of sulphides, that the process of deposition was a replacement process,that the mineral solutions were concentrated along channels or fissures due to faulting. The presence of silver in galena seems to show that ores were deposited from upward rising currents.

----- MINING.----

At present the larger part of the marketable fluorspar is taken out near the surface. When this is exhausted it is probable that some difficulty will be experienced in obtaining a supply of pure fluorspar, the reason being that the percentage of galena, blende,etc., which may be considered as impurities, so far as fluorspar is concerned, increases sensibly with depth, nor does the utilization of the fluorspar product of jigs, which also contains more or less sulphides, appear to solve the difficulty.

The system of working the mines has not been efficient or economical, and in a number of cases consists of mere makeshifts, rendered necessary by lack of capital. The vein matter is mined in open cuts and drifts, little attempt at systematic stoping has been made. The largest vein so far discovered in the state is owned by the Kentucky Fluorspar Company of Marion , Kentucky, and is known as mine No.1. It is situated on the side of a hill and runs almost due north and south from 25 to 50 feet below the ridge. It has been prospected for a distance of over 1200 feet and the width varies from 15 to 30 feet. In this case the spar is found from the grass roots down.

The main shaft of this mine is thirteen feet squareand has reached a depth of 106 feet. At this level two drifts, each six feet high by seven feet wide, are being run north and south alongt the vein, cutting through an almost solid mass of pure white fluorspar. Heavy timbers are

necessary to support the roofs. When a drift has been run far enough, a narrow track is laid, upon which small flat cars run. The buckets are placed on these, and when loaded at the end of the drift are wheeled to the foot of the shaft. They are then hoisted to the top by a horse power whim, so arranged that while one bucket is being brought up another is going down.

PREPARATION FOR MARKET.

Upon reaching the top the bucket is put on another car, wheeled to the sorting and cleaning sheds, dumped and returned for another load. At the sheds it is thoroughly washed by playing a hose on it, then it is taken in hand by the sorters, hackers, screeners, and barrellers. The large pure white lumps from 5 to 150 pounds in weight are first selected and turned over to the hackers, who chop off with hatchets the small amount of dirt adhering. It is then graded as No.1 pure white lump fluorspar and is used for the manu facture of hydro-fluoric acid and for grinding for use of glass manufacturers, enamelers, etc. It is ground usually in a buhr stone mill. It is difficult to grind, and requires considerable care and skill to produce a uniform grade and prevent clogging.

After taking out the large lumps the spar passes to the screeners who separate the fine or gravel spar from the crushed or small lump fluorspar by use of coarse screens. The crushed fluorspar is passed to the barrellers, who grade it into Nos. 1, 2, 3, according to the color and at the same time barrel it. Grade No.2 contains more or less galena, blende, calespar, and limestone country rock. Care is taken to keep the percentage of sulphides as low as possible, for the reason that this grade is most used by the smelters. Grade No. 3 might be classed as lead ore, it is crushed at the mills and run over jigs, where the galena is separated. This is sold to the smelters, and forms a considerable portion of revenue derived from the mines.

The crushrd fluorspar that comes over the jigs is marketed at the same price as grade No.2. There does not appear to be as clean separation made as there should be with two minerals of so different specific gravities, but it is very likely that this can be remedied by a little more skill on the part of the jigman. The separation of the blende and the fluorspar is impossible by the means of a jig, because of the nearness of the specifac gravities of the two minerals. Many men are working on this problem and already several promising if not satisfactory processes have been patented. A plant to do this work has just been completed in Paducah and another is being erected in St.Louis, while a third ~~ix~~ process is being perfected at a plant near Salem, Kentucky. It seems that a good separation could be got by taking advantage of the fact,that fluorspar will decrepitate when heated, especially where coarse blende is found. By crushing the ore to a uniform size, then heating, the fluorspar will break up into smaller pieces, and the ore could be sieved or run over jigs. The writer was informed that experiments along this line, were made at the Mass. Inst. of Technology, but was unable to get any data on the tests for the reason that the information discovered, had been bought by some mining company and was to be kept secret. The The writer does not think that it would be possible to separate the fine grained blende from the fluorspar by the decrepitation process, for the reason that the one would have to be crushed too fine before could get a uniform product.

Chemical analysis of the three grades:- As has previously been stated the fluorspar is divided up into three grades, according to quality. Results of a chemical analysis are as follows:

Grade	#1	#2	#3
Iron oxide	0.24%	1.32%	6.72%
Silica	0.10%	3.47%	10.12%
Alumina	1.12%	1.90%	3.13%
Fluorspar(CaF_2)	98.56%	89.96%	69.02%
Lead	0.00%	1.20%	6.24%
Zinc	0.00%	0.62%	2.14%
Sulphur	0.00%	0.76%	1.52%
	100.02%	99.23%	99.13%

The fluorspar found in this district is the richest ever found in the known world; It assays from 95% to 99.86% fluoride of calcium known as #1 fluorspar. The fluor spar of England and Germany rarely reaches 45% fluoride of calcium. The zinc produced in this district is of high grade assaying from 62% to 65 % metallic zinc and less than 1% iron.

THE USES OF FLUORSPAR.

The open hearth steel producers consume about eight pounds of fluorspar to every pound of steel. This in itself has caused a demand for the Kentucky fluorspar that is taxing the energies of several thousand men employed by the different compabies operating in the district.

Its province in the open hearth process is to eliminate sulphur and phosphorus in the various grades of iron, thus permitting the use of more scrap and lower grades of pig iron. The peculiar qualities of fluorspar in reaching a temperature far above its surroundings, renders it peculiarly valuable in the open hearth furnace, in the cupola of the foundryman or in the blast furnace of the iron producer. In case of clogging, a pasty slag, or a "freeze", a shovel or two of fluorspar relieves the over burdened furnace as well as the strain on the furnaceman.

The iron ores of the south,especially of the Alabama region, do not make a first class pig iron. The percentage of sulphur and phosphorus present in the ores, as well as sulphur in the coal, will invariably find its lodgement to a very great extent in the iron itself. The white sulphurous , phosphorus iron must always sell in a marked degree under the prices made for a soft gray product.

Fluorspar will remedy this; its action in eliminating sulphur and phosphorus through slagging and volatilization, will make thes southern ores into as valuable iron as the ores in the north.

INCREASING USE OF FLUORSPAR IN METALLURGICAL WORK.

Sometime ago Dr.Foehr, a noted German chemist and metallurgist, called attention in an article in the "Chemical Zeitung" to the growing tendency to return to the use of fluorspar as a flux in metallurgical operations. He stated that until the beginning of this century fluorspar was considered indispensable, but was replaced to a large extent by limestone, on account of being apparently much cheaper. The two fluxes, however, are so different in their action, even when accomplishing somewhat similar results, that no comparison is just when based merely on the relative price per ton.

In the United States fluorspar has probably never been used to the same extent as in England and on the continent, and for this, two reasons may be assigned: The lack of information as to its value and proper manner of using it to obtain good results, and the uncertainty of the supply. The latter cause no longer exists, as extensive and more workable deposits are now opened up in Kentucky.

The use of fluorspar in metallugical work may be considered under five heads. (1) In the blast furnace, especially for the production of ferro-silicon and ferro-manganese; (2) In the open hearth steel furnace, especially with the basic process,to make more fluid the slag, to help carry off phosphorus and reduce the sulphur; (3) In the foundry cupola, to make iron more fluid, permit the use of greater quantities of lower grades and scrap iron, and to reduce impurities; (4) In crucible and brass foundries,to make the meta l more fluid; (5) In the metallurgy of aluminum, whereit makes a good flux for the metal in connection with cryolite or common salt.

In the blast furnace the smelting of very refractory ores is impossible, almost, without the use of fluorspar. But even with good ores there are advantages in the use of fluorspar and which do not appear at the first glance. Thus the reaction of fluorspar and limestone respectively are as follows:-

$$2\ Ca\ F_2 + 3\ Si\ O_2 = 2\ Ca\ Si\ O_3 + Si\ F_2$$
$$3\ Ca\ CO_3 + 3\ Si\ O_2 = 3\ Ca\ Si\ O_3 + 3\ CO_2$$

These formulae show a quantitative economy in favor of fluorspar of 300 to 156. But Dr. Foehr, who has already been quoted, claims that one part of fluorspar goes further than ten parts of limestone. The fluorspar reduces the quantity of fuel required, forming but two parts of slag where limestone forms three, and it is probable that it forms fluor silicate, wherby heat is likely to be liberated. When it is blown into the tuyeres it forms an energetic solvent. In the manufacture of ferro-silicon, an iron containing 10% silicon may be obtained in an ordinary blast furnace from the siliceous ores if fluxed with fluorspar and the slag is strongly basic. The fluorspar first reduces the silicon energetically forming fluor silicon, and this is then reduced to silicon by the hydrogen of the furnace gasses and possibly also by coke. A peculiarity of fluorspar is its property of reducing the most different bodies it being also advantageous in the manufacture of spiegeleisen, using a manganese combination and fluorspar. In this case a very basic slag, rich in fluorides, is desirable. In Basic open-hearth steel plants in the United States the use of fluorspar is steadily growing, its main function being to render more fluid the slag, not only on the hearth, but in the ladle and mould as well. In the Krupp and Rollet methods of dephosphorizing pig in basic-lined cupolas fluorspar is used to carry phosphorus into the slag.

In foundry work the value of fluorspar as a fluxing agent seems to have been discovered first by the manufacturers of chilled car wheels. Unlike chill rolls, car wheels are cast from iron melted in a cupola, while limestone is used in cupola work, its function is merely to slag off the ashes of the fuel. It has no important chemical action on the iron, excepting the important one of tending to slag the silicon. Fluorspar, while accomplishing all that limestone does in fluxing off the ashes with a smaller quantity, has an important effect on the iron, keeping it gray and soft by holding the silicon as an alloy, while it tends to carry some phosphorus and sulphur into the slag. In such work as the manufacture of car wheels, where low silicon iron is necessary, the advantages

of fluorspar have been first appreciated, but in other work its use may be very advantageous, permitting the use of a greater quantity of scrap without unfavorably affecting the melting ratio, and permitting also the use of lower grades of iron for melting. The best results seem to obtained when about one-third of one percent is employed, while beyond one-half percent the results are distinctlt inferior for certain classes of work, one reason of which is that the larger quantity of fluorspar ~~ted~~ tends to hold manganese contained in iron from slagging. In other classe of work much larger quantities of fluorspar may be employed tp reduce th the quantity of slag and make iron more fluid. In English foundaries the use of this flux is much more common than in the United States.

USE IN GLASS MAKING.

Hundreds of tons of fluorspar are used by the glass makers, especially those that manufacture plate glass or any clear and brilliant product. The action of fluorspar in the melting pot has caused a perfection to be reached in American glass manufacture that a few years ago would have been considered impossible. American plate glass and American cut glass is not only on par with the French, but thanks to the element fluorine, it has given our glass a finish and brilliancy that no other glass can equal without the use of fluorspar in its production.

USE IN ACID MANUFACTURE.

Kentucky provides the hydrofluoric acid makers with the chemically pure ground product from its snow-white selected fluorspar. When it is considered that a slight admixture of sand or silica will cause chemical reactions in the production of this acid that changes almost its entire nature, the larger quantity used by the acid makers, speaks volumes for the purity of the Kentucky product.